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CORROSION PRODUCT SEPARATION IN A CROLOY 9M MERCURY LOOP

Fourth Quarterly Report

By

D. B. Cooper and E. J. Vargo

Prepared For

National Aeronautics and Space Administration

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Materials Technology
TRW Electromechanical Division
THOMPSON RAMO WOOLDRIDGE INC.
23555 Euclid Avenue
Cleveland, Ohio 44117

TECHNICAL MEMORANDUM

TM 3928

CORROSION PRODUCT SEPARATION IN A CROLOY 9M MERCURY LOOP

By

D. B. Cooper and E. J. Vargo
Materials Research & Development

Fourth Quarterly Report
Covering the Period February 1, 1964 through April 30, 1964

Prepared For

National Aeronautics and Space Administration

Contract No. NAS 3-2538

Technical Management

NASA - Lewis Research Center

SNAP 8 Project Office
P. L. Stone

May 11, 1964

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

TM 3928

INTRODUCTION

The containment of mercury in a mercury Rankine cycle power system is a serious materials problem. The problem is critical not only because of the corrosive penetration by mercury but also because of the generation of corrosion products and their subsequent mass transfer to sections of the system which are sensitive to deposition of these products.

One of several materials which have indicated more corrosion resistance to mercury than others is a chromium alloy steel known as Croloy 9M*. Capsule tests have yielded data which indicated that for temperatures below 1200°F the corrosion resistance of this material may be adequate for a Rankine cycle turbo-generator power system. However, it is recognized that corrosion products still may be generated in a Croloy 9M mercury system to such an extent that the flow of the working fluid could be blocked eventually by mass transfer.

The continuous separation of the corrosion products from the working fluid appears to be the most feasible method to avoid mass transfer difficulties. The fabrication of a forced circulation loop has been completed and operation has been initiated in order to explore the engineering concept of corrosion product separation by hot trapping and magnetic means and also to evaluate the corrosion resistance of Croloy 9M.

This work is sponsored by the National Aeronautics and Space Administration under Contract No. NAS 3-2538. This report is the fourth quarterly progress report and covers the period from February 1, 1964 through April 30, 1964.

*Nominal analysis: Cr 8.0 - 10.0
Mo 0.9 - 1.1
C 0.15

PROJECT OBJECTIVES FOR THE REPORTING PERIOD

Operation of the loop was to be continued towards the 2950-hour duration (giving a total of 2500 hours since the installation of the orifice). Evaluation of the throttling valve was to be continued.

PROJECT PROGRESS DURING THE REPORTING PERIOD

The loop operated very satisfactorily during the first part of the quarter until a total of 960 hours of operation had been accumulated. At this time the flow increased from 65 pounds per hour to 75 pounds per hour rather abruptly. As a result of the increased flow, the boiler temperature decreased, and the temperatures on the condenser side of the loop increased. After another five hours of operation, the flow again increased abruptly, stabilizing at 105 pounds per hour, with a second decrease in boiler temperature and increase in condenser-side temperatures. At this time it was also observed that the level on the condenser-side had decreased. Approximately 25 pounds of mercury were added to the loop to increase the condenser level. In order to correct the temperature profile, the power to the boiler was increased and the condenser cooling was increased to its maximum. These changes seemed to correct the situation for a short time, but the level in the condenser decreased again over a period of several hours. Approximately another 25 pounds of mercury were added to the loop, and this resulted in stable operating conditions at a flow rate of approximately 100 pounds per hour. All conditions were satisfactory with the exception of the vapor trap outlet temperature which indicated that this area contained some liquid mercury. It was decided to allow the loop to operate with this condition for several days before making any further changes.

The only logical explanation for the abrupt changes in flow seemed to be that some restriction in the system, perhaps in the orifice, was removed with time, thus permitting a greater flow of mercury through the loop.

Since no mercury was lost to the atmosphere with decreases in the condenser level, and since this level eventually became stable, it was proposed that some cavity in the system had filled with mercury. The explanation for this is that a crack developed in the inner shell of the liquid corrosion product separator, allowing the magnet cavity to fill with mercury. In order to verify this and also to verify that the vapor trap outlet was wet, it was decided to take radiographs of the entire system. An iridium-192 source was employed, and the results indicated the following:

1) The vapor in the vapor trap contained some liquid mercury.

2) The exit tube from the vapor trap and the vapor corrosion product separator did not contain liquid mercury.

3) A crack had developed in the inner shell of the liquid corrosion product separator, since the magnet cavity was found to contain mercury.

4) The area between the exit of the vapor trap and the liquid level in the condenser contained no liquid mercury.

The boiler power was again increased, and the liquid level in the boiler was decreased in order to provide vapor of higher quality at the inlet of the vapor trap. These changes resulted in drying of the vapor in the vapor trap, as indicated by immersion thermocouples in the unit.

Following these changes, the loop operated without incident for an additional 762 hours until a total of 1722 hours of operation had been accumulated. At this time the heater on the superheater outlet failed and the loop was shut down. The heater was replaced, and the loop was restarted without difficulty.

Operation of the loop has continued from this point without incident. A total of 2765 hours have now been accumulated (448 of these hours were accumulated before the installation of the orifice). Operating conditions for the loop at present are shown schematically in Figure 1.

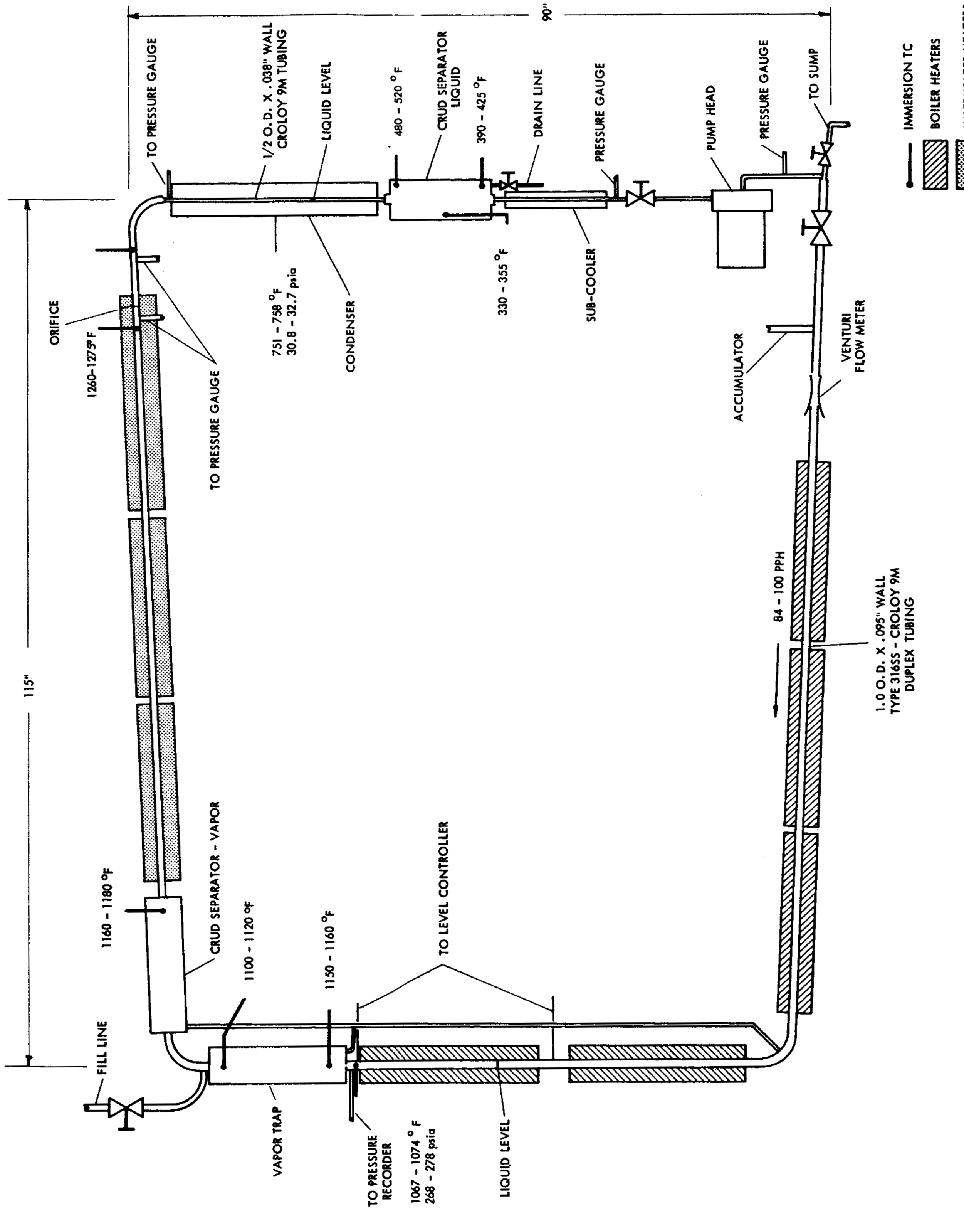


FIGURE 1. CROLOY 9M LOOP SCHEMATIC

1191

QUALITY ASSURANCE ACTIVITIES

Evaluation of the Croloy 9M throttling valve was completed. It will be recalled that a very severe leak developed in the valve after 448 hours of operation and that the valve was removed and replaced with a Croloy 9M orifice. During this period of operation, the average temperature on the inlet side of the valve was 1076°F (28°F superheat), while the average outlet temperature was 809°F (31°F superheat).

Disassembly of the valve revealed that failure was brought about by "freezing" of the handle to a threaded extension welded to the bellows. This resulted in twisting of the bellows and eventual failure. Figure 2 shows the disassembled valve, and Figure 3 shows the deformed bellows.

The valve was sectioned and mounted for metallographic evaluation. Examination showed that a deposit had formed on the outlet side of the orifice in the valve. Two foreign metallic chips were also found in this area of the valve. The combination of the deposit and metallic chips caused a considerable reduction in the flow passage in the valve. This explains the control difficulties experienced during initial loop operation when fine adjustment of the valve could not be obtained. Photomicrographs of this area of the valve are shown in Figures 4, 5, and 6.

An electron beam microanalysis was performed on the larger of the two metallic chips and on the deposit by Advanced Metals Research Corporation. A careful comparison of the iron, chromium, and molybdenum x-ray line intensities for the base alloy and the metallic chip revealed no significant differences, as seen in Figures 7 and 8. In addition, the manganese and silicon content of these two zones appeared to be identical. It is thus apparent that the metallic chip is Croloy 9M, probably a residual particle remaining in the valve after fabrication of this component.

The iron, chromium, and molybdenum distributions in the deposit are shown in Figures 9, 10, and 11, respectively. It is seen here that the deposit is iron-rich and chromium and molybdenum-poor. The chromium shows a small gradient in the vicinity of the deposit-base metal interface but rapidly falls to less than one percent. The molybdenum content drops abruptly to approximately zero percent at the deposit-base metal interface. The iron concentration rises to roughly 90 to 95 percent. Chromium-rich phases are present in both the deposit and the base metal as evidenced by the sharp intensity spikes. These phases are very likely carbides. The balance of 5 to 10 percent material not seen in the analysis (90 to 95 percent iron, approximately one percent chromium and molybdenum) is probably a result of the porosity in the deposit rather than the presence of an additional element.

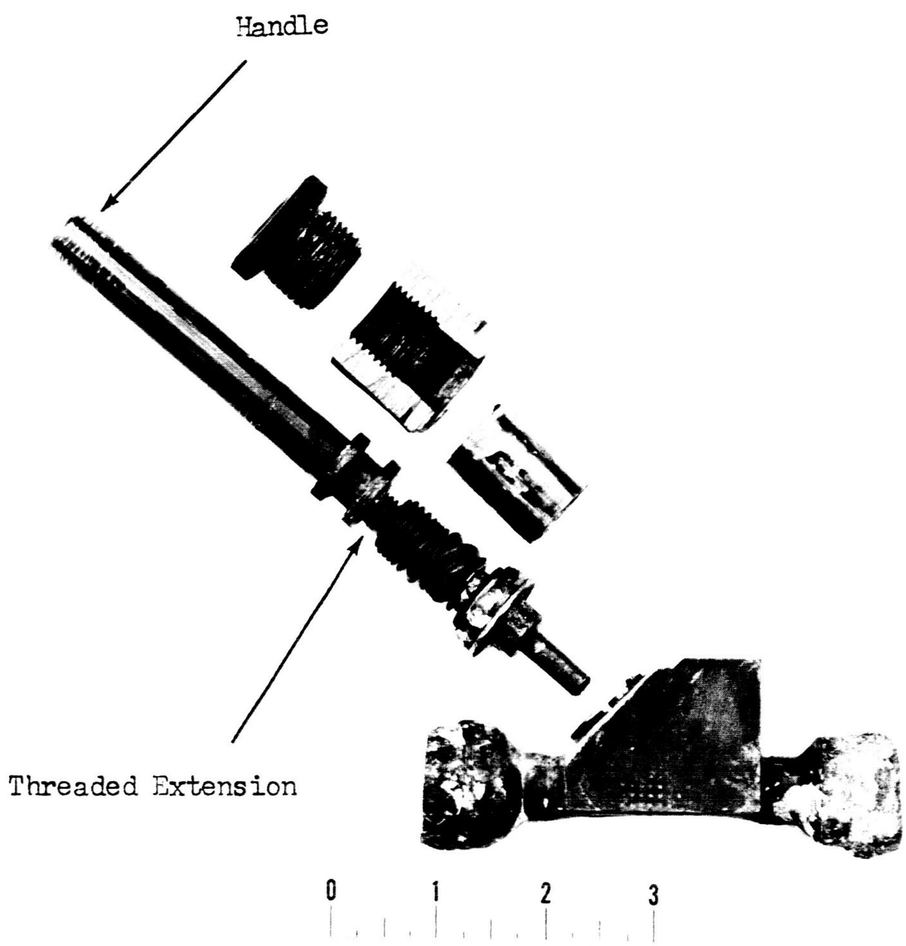
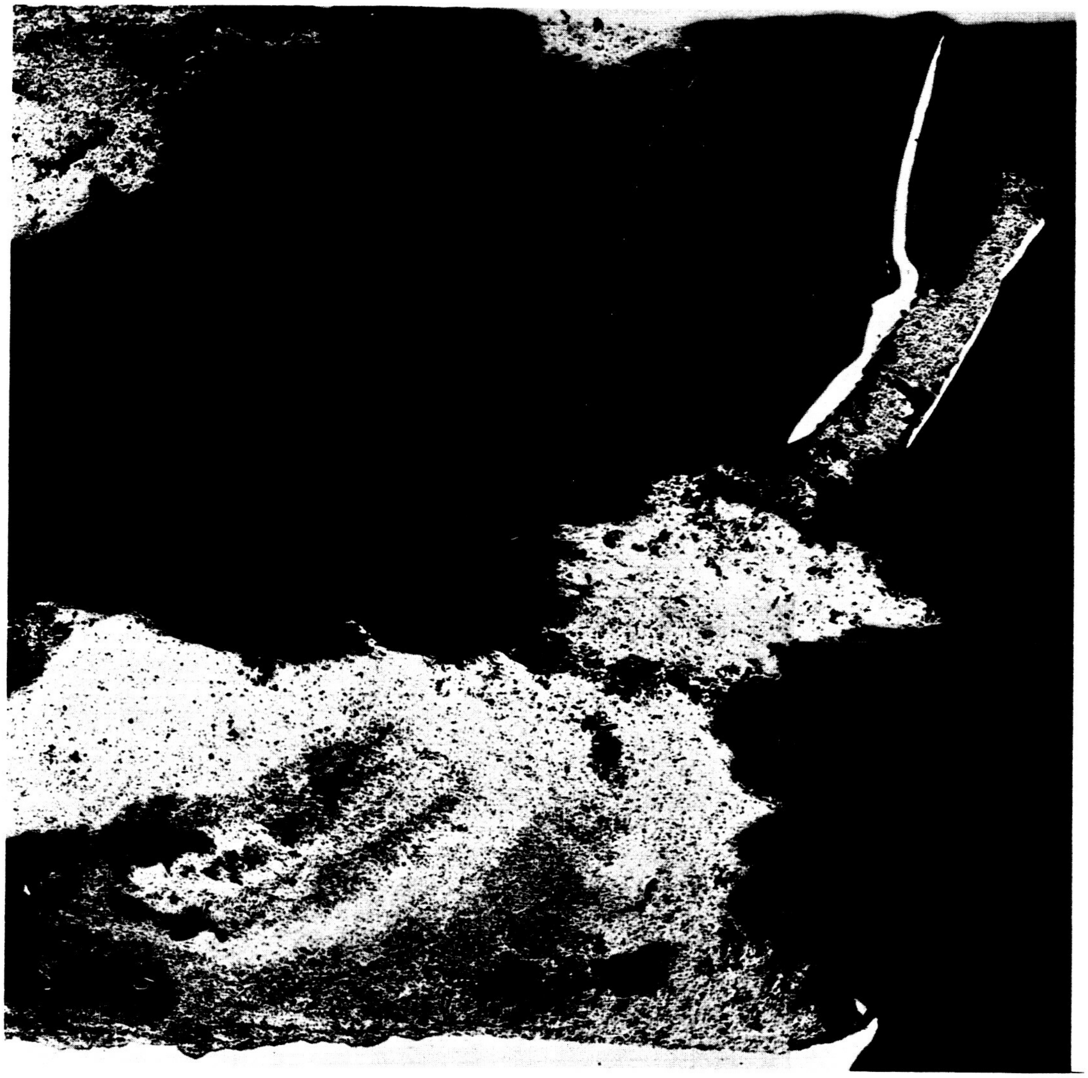


Figure 2. Disassembled Croloy 9M Throttling Valve

6013

3.2X

Figure 3. Type 321 SS Bellows from Croloy 9M Throttling Valve



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100X

Figure 4. Composite of Figures 5 and 6 Showing the Outlet Side of the Orifice in the Croloy 9M Throttling Valve.

6014

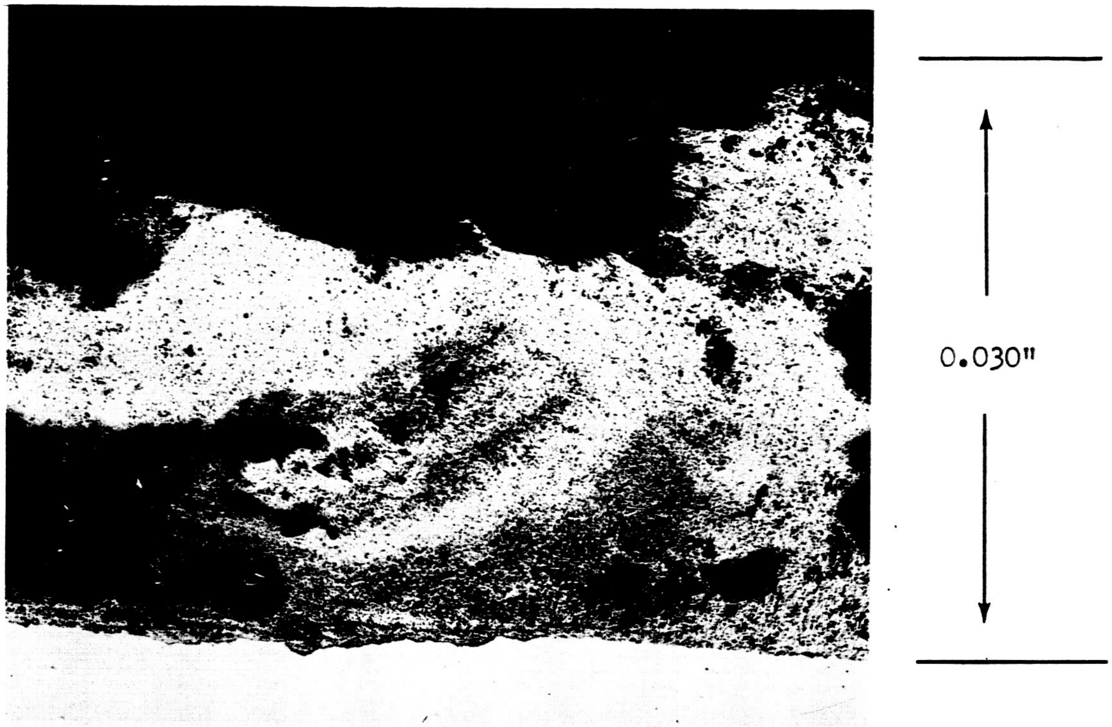

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Figure 5. Deposition on the Outlet Side of the Orifice in the Croloy 9M Throttling Valve

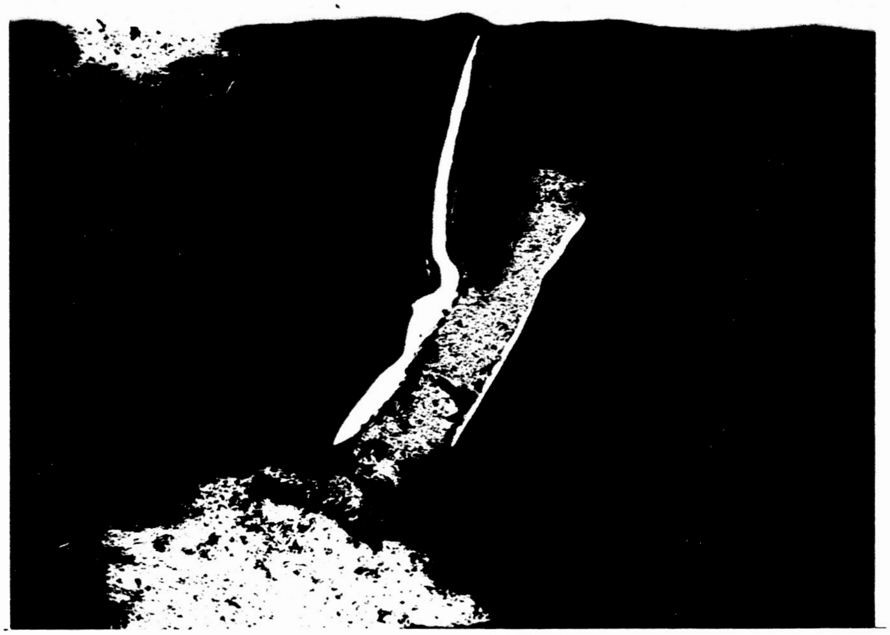

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Figure 6. Deposition and Metallic Chips on the Outlet Side of the Orifice in the Croloy 9M Throttling Valve.

TM 3928

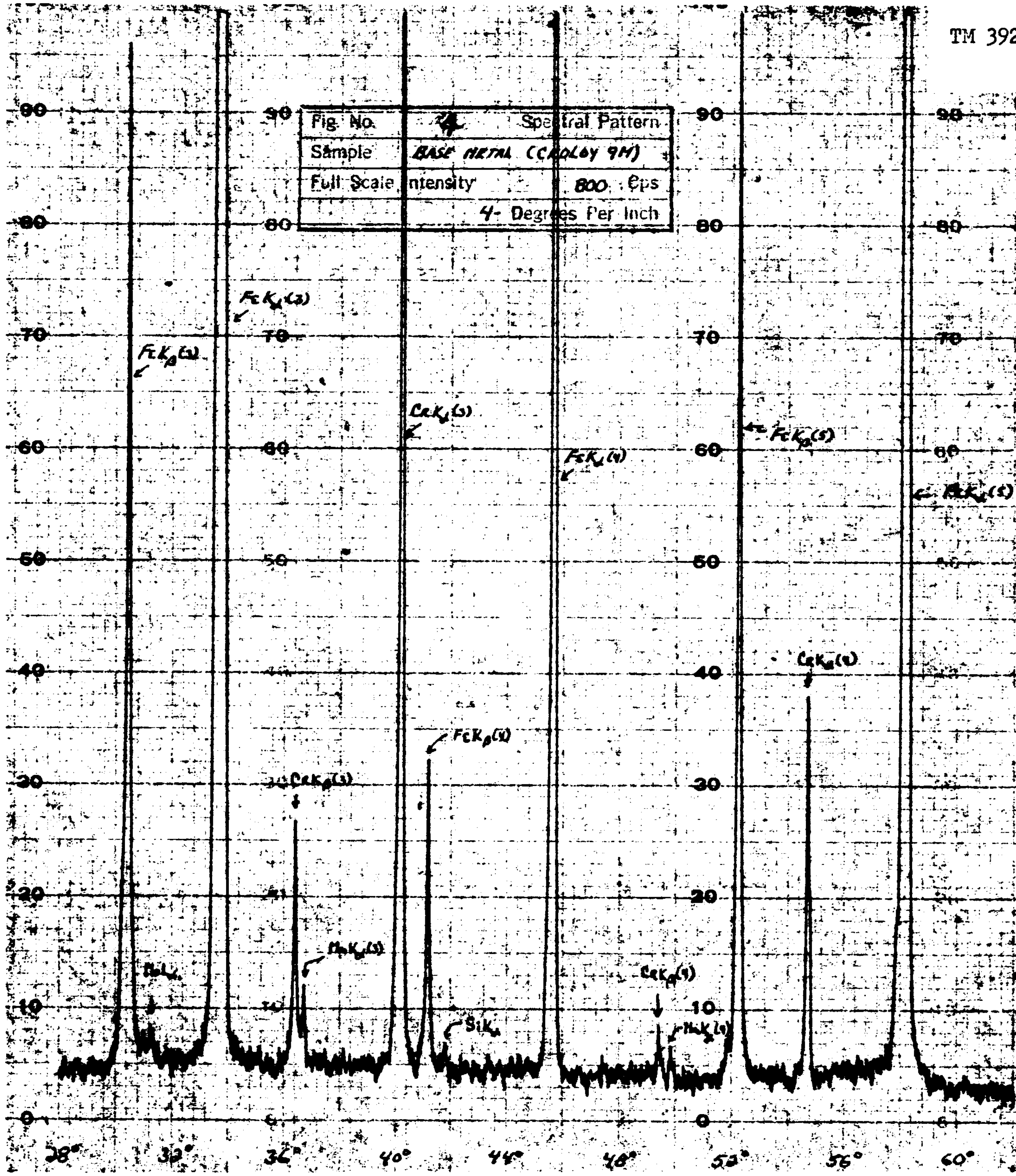

Figure 7. Spectral Pattern of Croloy 9M Base Metal

TM 3928

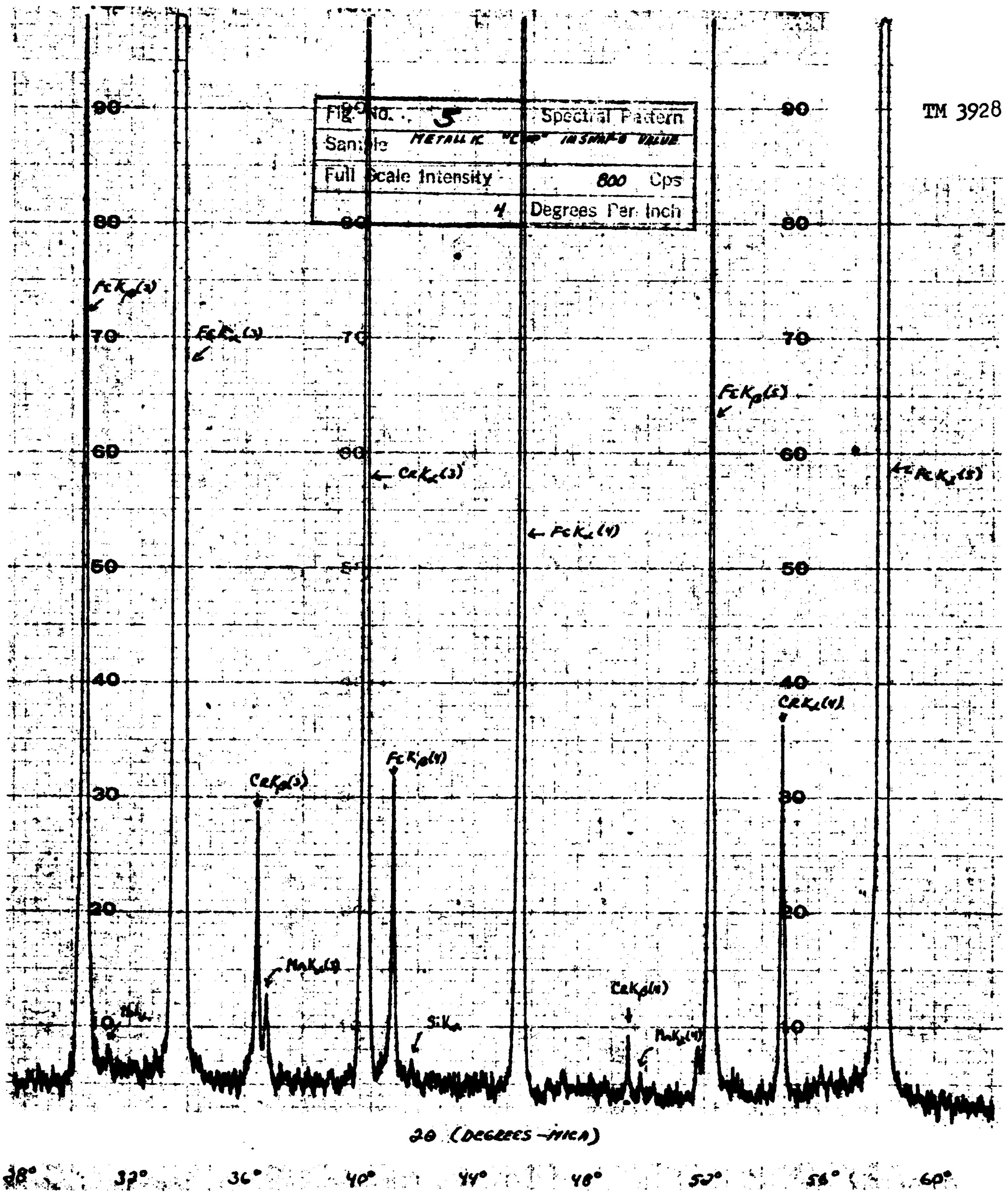

Figure 8. Spectral Pattern of the Metallic Chip Found in the Croloy 9M Throttling Valve

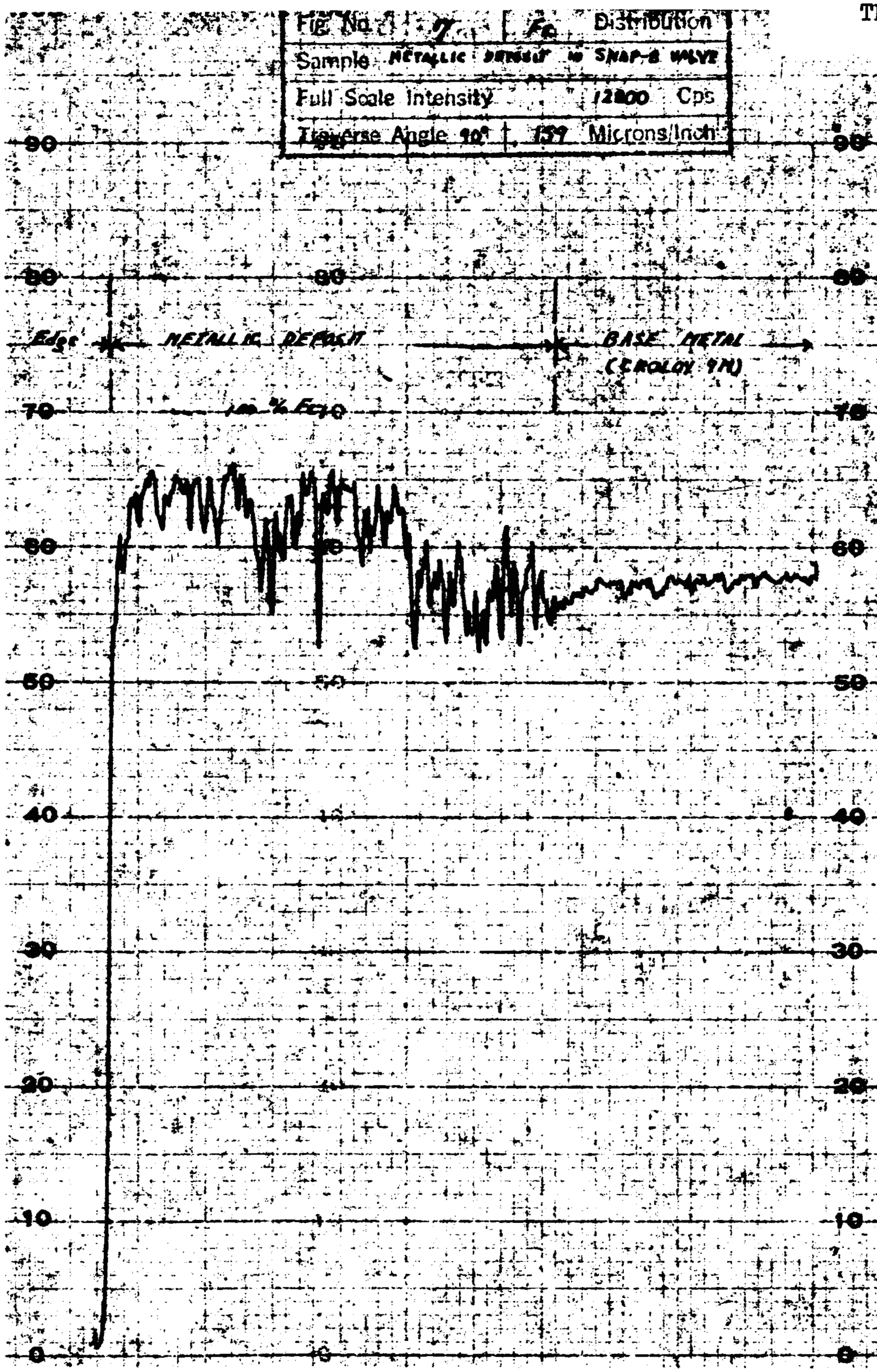

Figure 9. Distribution of Iron in the Deposit Found in the Croloy 9M Throttling Valve

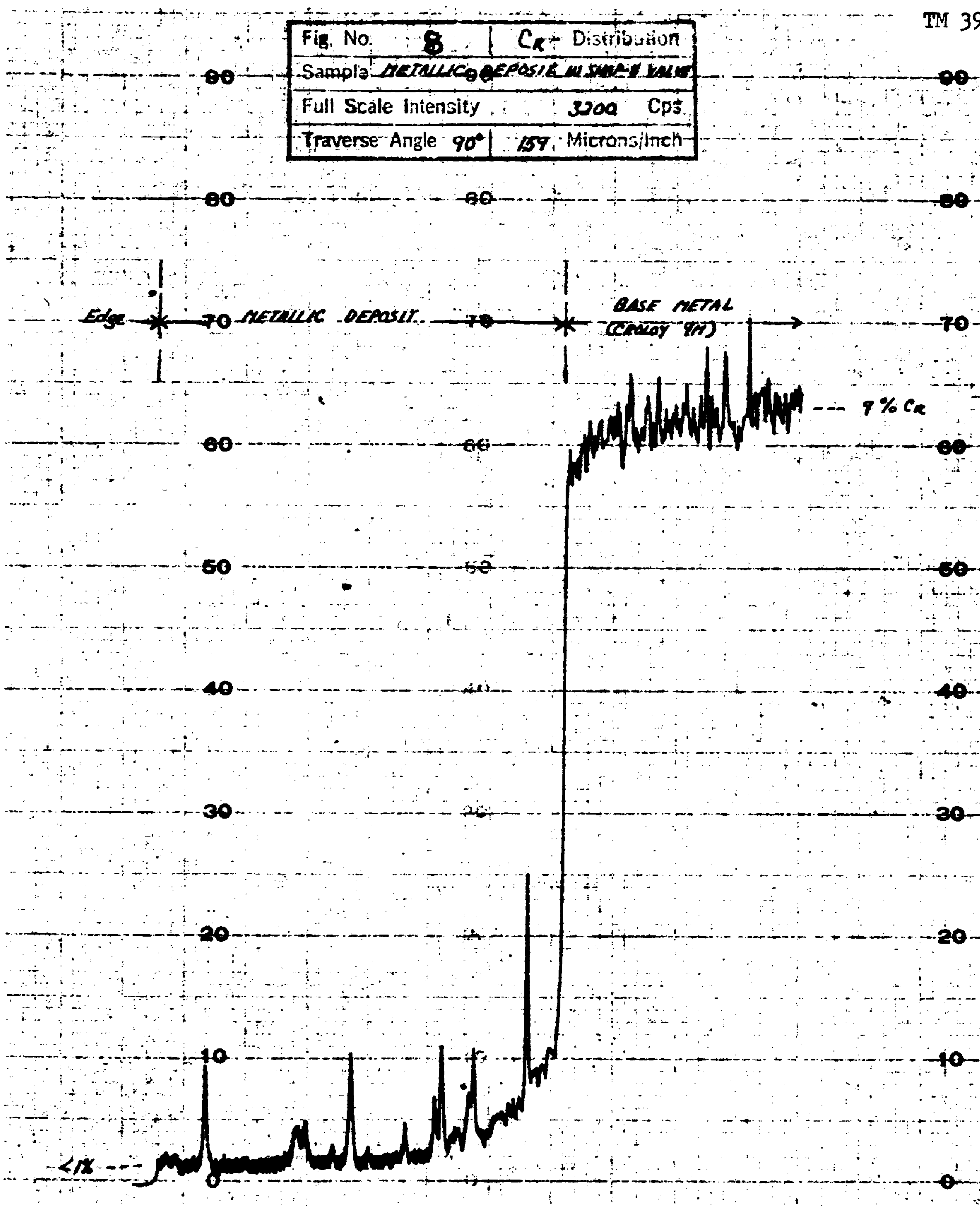

Figure 10. Distribution of Chromium in the Deposit Found in the Croloy 9M Throttling Valve

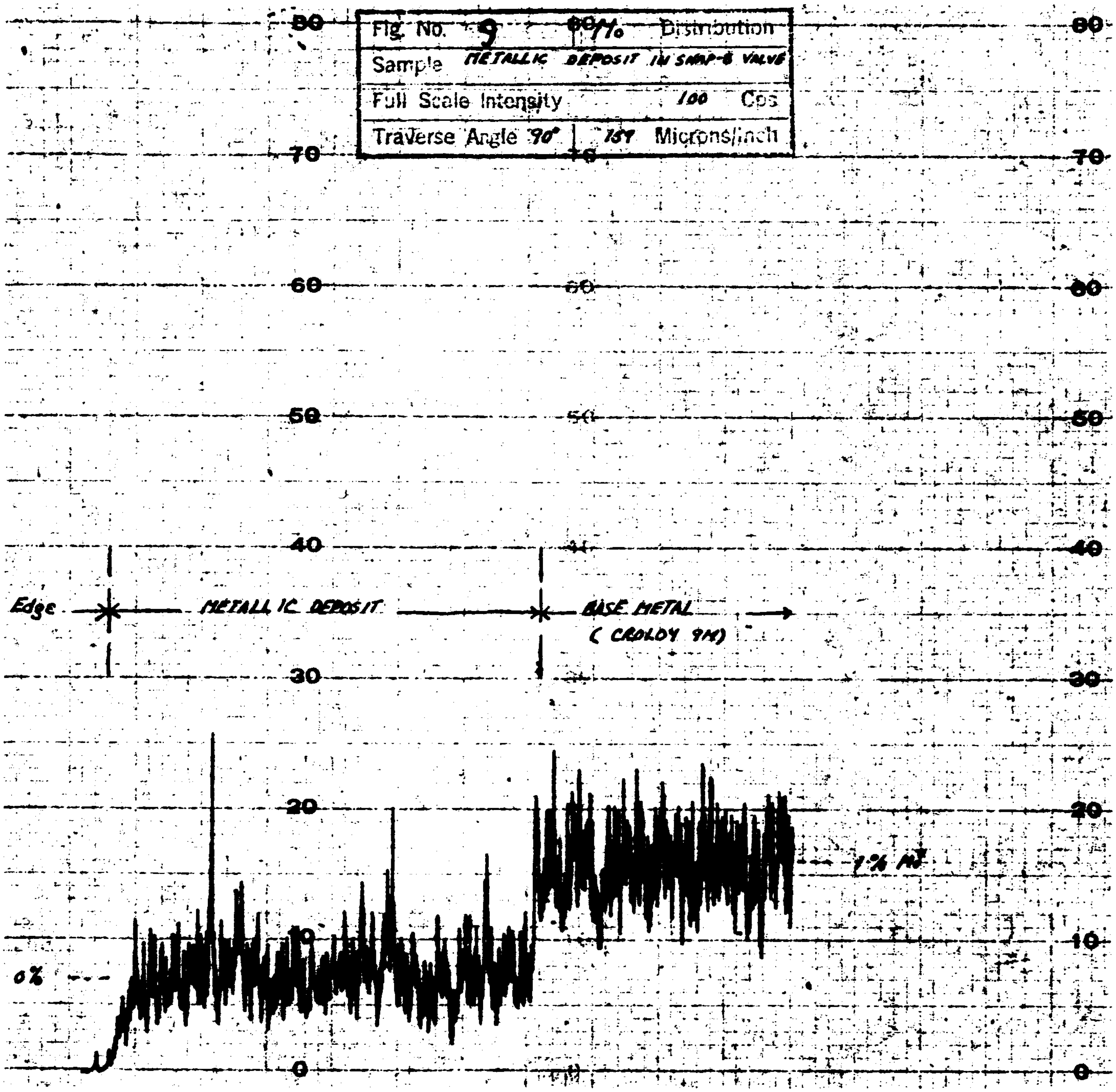

Figure 11. Distribution of Molybdenum in the Deposit Found in the Croloy 9M Throttling Valve

The sharp decrease in both the chromium and molybdenum at the deposit-base metal interface suggests that iron has been removed from another part of the system and has been transported to the throttling valve. Examination of the remainder of the system should yield further information on this theory.

The stem (Croloy 9M) and the bellows (Type 321 SS) from the valve were also examined metallographically. As seen in Figure 12, some slight deposition was observed on the valve stem. The stem also suffered some corrosion and/or erosion damage as shown in Figure 13. The maximum depth of attack was approximately four mils. Some slight attack ($<$ one mil) was also observed on the Type 321 SS bellows, as shown in Figure 14.

As requested by the NASA contracting officer, further information on the spectrographic analyses and mechanical tests performed during the last quarter are presented here.

During the shut-down period after 434 hours of operation, two representative samples of mercury were taken from the loop under a cover of argon. One sample was removed from the liquid corrosion product separator, and the second sample was taken from the remainder of the mercury in the system. Spectrographic analyses were conducted on the two samples. The samples were then exposed to air for three days in order to allow any corrosion products present to separate from the mercury. Upon exposure to air, no "scum" formed on the surface of the sample from the liquid corrosion product separator. A very small quantity of "scum" did form on the surface of the second sample and this was analyzed spectrographically. Following the shut-down after 448 hours of operation, a third representative sample was taken from the system. This sample was treated in the same manner as the other two. A small quantity of "scum" formed on the surface of this sample upon exposure to air. Results of the spectrographic analyses are presented in Table 1.

The results of tensile tests performed on the as-rolled Croloy 9M sheets are presented in Table 2. Two samples were machined from each of two sheets and were tested at room temperature.

PROBLEM AREAS

No problems exist at the present time.

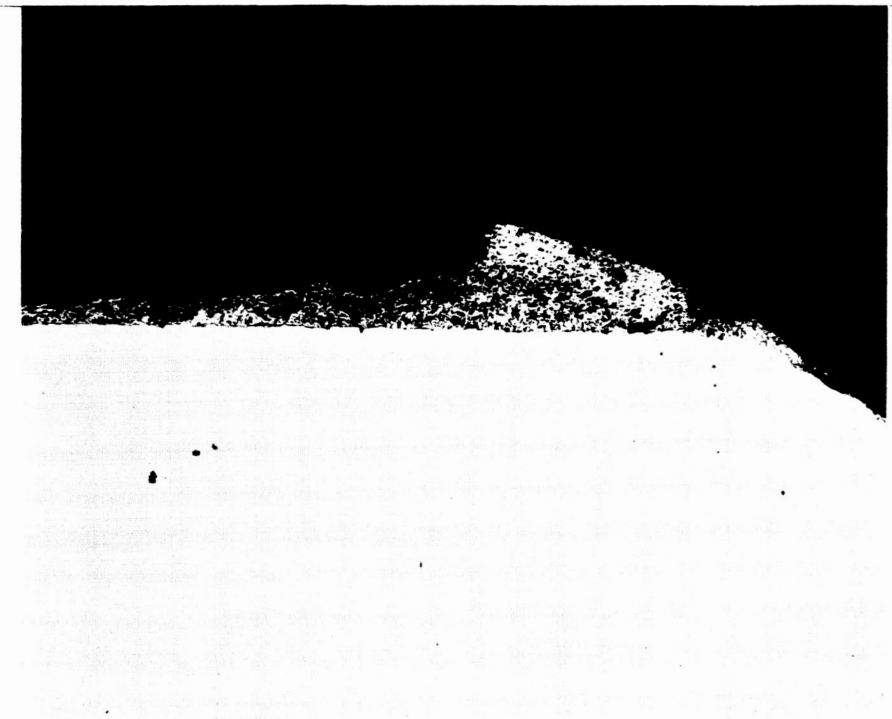

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Figure 12. Deposition on the Stem of the Croloy 9M Throttling Valve

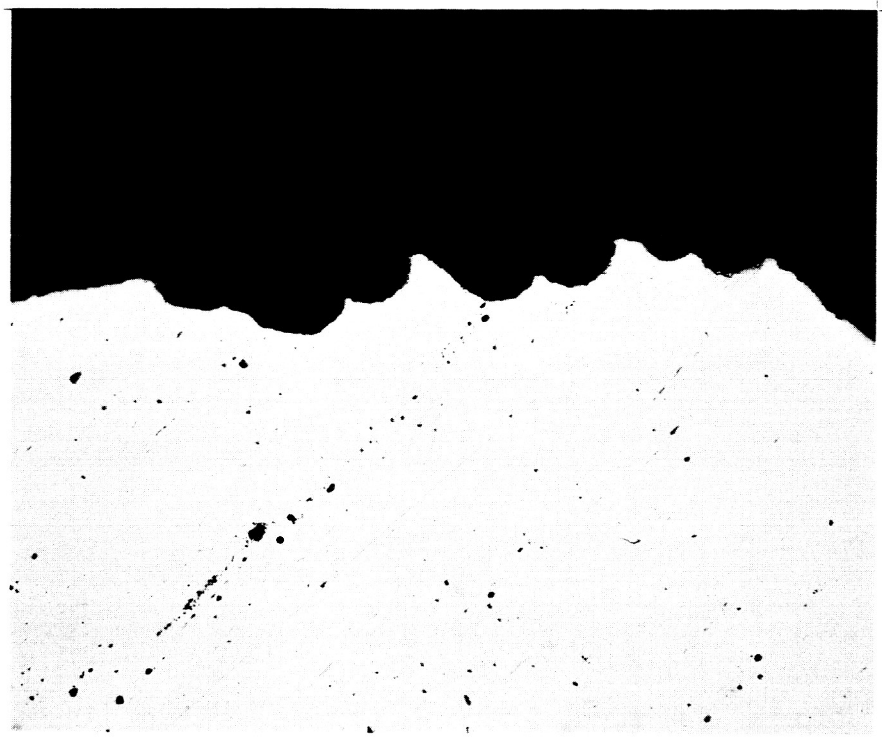

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Figure 13. Attack on the Stem of the Croloy 9M Throttling Valve

6017

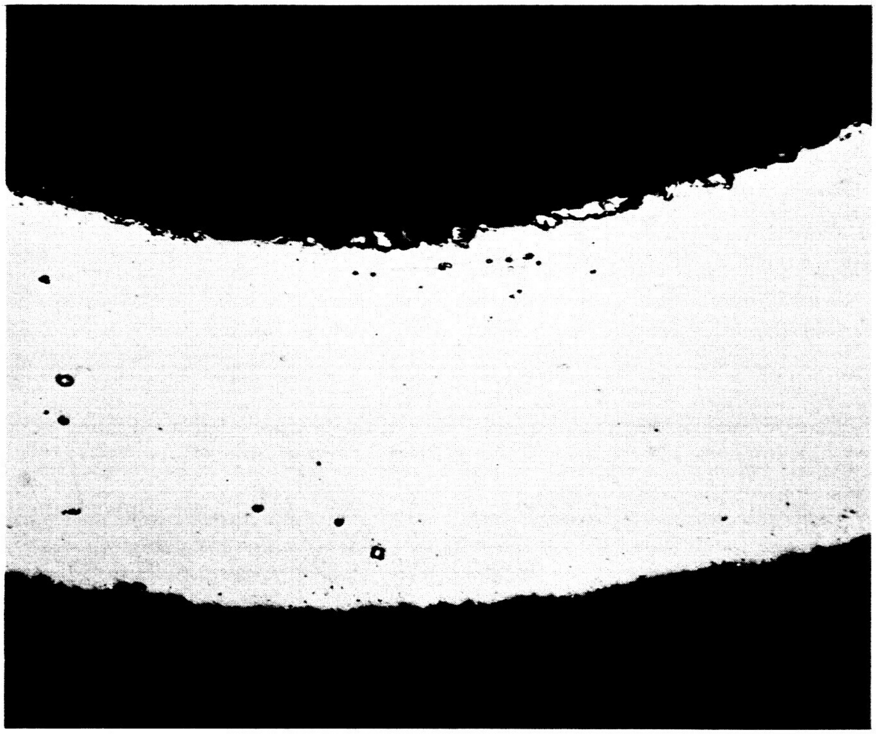

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Figure 14. Section of the Type 321 SS Bellows from the Croloy 9M Throttling Valve

PLANNED DIRECTION OF EFFORT FOR THE NEXT QUARTER

The loop will be shut down and disassembled. Specimens will be removed from the system and evaluated. Writing of the final report will be completed.

TABLE 1

SPECTROGRAPHIC ANALYSIS OF MERCURY SAMPLES

A. Sample from Liquid Corrosion Product Separator - 434 Hours

Faint trace	-	Ca

B. Sample from Remainder of System - 434 Hours

Mercury:

Minor	-	Ag
Faint trace	-	Ca

Scum:

Appreciable	-	Cu
Minor	-	Ca, Mg
Trace to minor	-	Cr, Ni
Trace	-	B, Si, Fe
Faint trace	-	Al, Mo

C. Sample Removed from Entire System - 448 Hours

Mercury:

Trace to minor	-	Ag
Faint trace	-	Ca, Cu, Mg

Scum:

Minor	-	Cu, Sn
Trace to minor	-	Ca, Mg
Trace	-	Al, Ag, Cd, Fe, Pb, Si

TABLE 2

TENSILE TESTS OF CROLOY 9M SHEET SPECIMENS

	Sheet 1		Sheet 2	
	A	B	A	B
Ultimate strength, psi	124,800	108,000	89,600	90,600
0.2% Offset Yield strength, psi	83,700	71,300	57,000	54,800
Percent Elongation in 2 Inches	27.0	18.5	35.3	34.8
Percent Reduction of Area	63.1	43.9	75.0	47.4

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